Superconductivity near 70 K in a new family of layered copper oxides

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A new family of high-temperature superconductors is described, with the general formula $Pb_2Sr_2ACu_3O_{8+\delta}$. Although they have the planes of CuO_5 square pyramids characteristic of the other copper-oxide superconductors, the new compounds belong to a distinct structural series, with wide scope for elemental substitution. Their unusual electronic configuration also gives new insight into the role of charge distribution among the structural building blocks in controlling superconductivity.

SINCE the first observation[1] of high-transition-temperature (high-T_c) superconductivity in La-Ba-Cu-O, progress in the understanding of this remarkable phenomenon has been coupled to the discovery of new materials. Until now, three families of copper-oxide-based high-T_c superconductors have been identified, based on $(La,M)_2CuO_4$, $LnBa_2Cu_3O_7$, and $(Tl,Bi)_m(Ba,Sr)_2Ca_{n+1}Cu_nO_{m+2n+2}$ (ref. 2). (Here M represents a metal cation that may substitute on some La sites, and Ln represents a lanthanide.) Here we report the discovery of a new family of planar copper-oxide superconductors with general formula $Pb_2Sr_2ACu_3O_{8+\delta}$ (where A is a lanthanide or a mixture of Ln+Sr or Ca), and describe the synthesis, crystal structure and properties of prototype compounds. We find, for example, that one preliminary optimal composition $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$ has a superconducting T_c of 68 K. The new family displays the same kind of rich substitutional chemistry as is observed for $LnBa_2Cu_3O_7$, with the phase forming for Y and at least La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb and Lu, spanning the entire rare-earth series. Wide ranges of large-metal-atom solid solution and oxygen stoichiometry are observed, suggesting many possible avenues to be explored for the optimization of superconducting properties.

Superconductivity is induced in the host compounds $Pb_2Sr_2LnCu_3O_{8+\delta}$ ($\delta=0$) either by partial substitution of a divalent ion (such as Sr or Ca) on the lanthanide site, or possibly by the accommodation of excess oxygen ($\delta>0$), or a combination of both. The compounds can be synthesized only under mildly reducing conditions, which are necessary to maintain Pb in a 2+ oxidation state. Oxidation of $\delta=0$ compounds is possible, but only at low temperatures, where decomposition to a Pb(IV)-containing perovskite is sluggish. Remarkably, the formal average oxidation state of copper in the superconductors is less than 2+, but a clear structural distinction between different types of copper layers leads us to hypothesize that holes are nonetheless present on electronically active CuO pyramidal planes.

Synthesis

The preparative conditions for the new materials are considerably more stringent than for the previously known copper-based superconductors. Direct synthesis of members of this family by reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 900 °C is not possible because of the stability of the oxidized $SrPbO_3$-based perovskite. Successful synthesis is accomplished by the reaction of PbO with prereacted (Sr, Ca, Ln) oxide precursors. The precursors are prepared from oxides and carbonates in the appropriate metal ratios, calcined for 16 hours (in dense Al_2O_3 crucibles) at 920-980 °C in air with one intermediate grinding. Some of the $Pb_2Sr_2LnCu_3O_{8+\delta}$ compounds can be prepared in air from $PbO+LnSr_2Cu_3O_x$ precursor mixtures, which are not reacted at temperatures below ~850 °C. For example, single-phase $Pb_2Sr_2YCu_3O_{8+\delta}$ ($\delta=0$) can be prepared by reacting PbO with $YSr_2Cu_3O_x$ at 920 °C for 1 h, followed by quenching. Slower cooling results in partial decomposition through oxidation. Short reaction times are generally sufficient to obtain single-phase products. The same air-heating/quenching process does not appear to work, however, for $Pb_2Sr_2LaCu_3O_{8+\delta}$ or $Pb_2Sr_2LuCu_3O_{8+\delta}$.

The best synthetic conditions found so far involve the reaction of PbO with the cuprate precursors in thoroughly mixed pressed pellets. Reaction temperatures are between 860 and 925 °C, for times between 1-16 h, in a flowing gas stream of 1% O_2 in N_2, a mildly reducing atmosphere. For $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$, for example, single-phase materials are obtained for $0\le x<0.5$ in 1% O_2 after heating overnight at 865 °C and cooling in the gas stream to room temperature in 15 minutes. Using higher temperatures, higher p_{O_2} in the gas stream or higher Ca contents of the starting mixture results in the intergrowth of 123-type $YSr_2(Pb,Cu)_3O_x$ with the new compound, or the formation of an $SrPbO_3$-based second phase. Similar procedures are successful for other Sr/rare-earth/Ca combinations. The oxygen contents of $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$ for $0\le x\le 0.50$, prepared under these conditions, are measured by reduction in H_2 and are uniformly $\delta=0\pm0.1$. Ca is employed as a dopant on the Ln site because it has an ionic size similar to the intermediate rare-earths. We have not yet found synthetic conditions under which $Pb_2Sr_{2+x}Ln_{1-x}Cu_3O_{8+\delta}$ solid solutions can be prepared as single-phase polycrystalline samples that are good bulk superconductors, although superconducting single crystals of that stoichiometry have been prepared.

Single crystals of the superconducting compounds were grown from PbO- and CuO-rich melts using a similar precursor technique. Melt compositions were generally $Pb_{3.5}Sr_3YCu_4O_x$. Following a 30-min soak at 1,025 °C, samples were cooled at 2 °C min^{-1} in the 1% O_2 atmosphere to temperatures between 800 and 400 °C, and were then rapidly cooled to room temperature in the same gas stream. Crystals are plate-like in habit, but are generally more equiaxed than those of $LnBa_2Cu_3O_7$.

Stoichiometry and crystal structure

Compounds of stoichiometry $Pb_2Sr_2LnCu_3O_8$ ($\delta=0$) are not bulk superconductors, although we often observe small amounts of superconductivity (1% or less) in materials of that stoichiometry prepared either by the quench or by the 1%-O_2 synthetic techniques. The non-bulk superconductivity may be due to inhomogeneities in either oxygen content or Sr/Ln distribution.

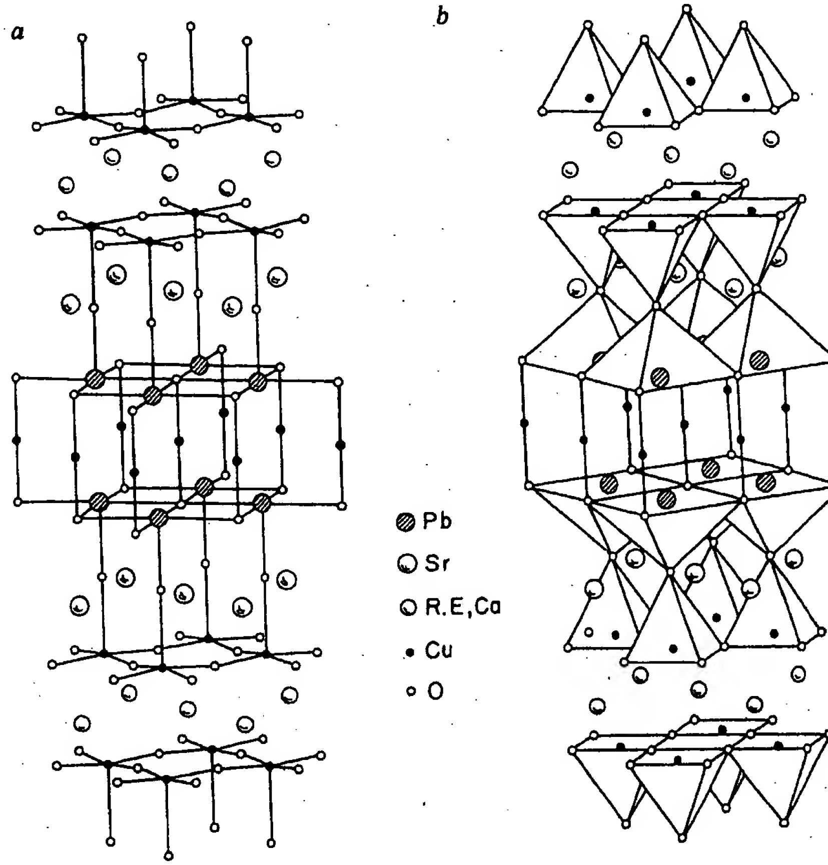

Fig. 1 Two representations of the crystal structure for the new superconducting compounds, for the case of $Pb_2Sr_{2.24}Nd_{0.76}Cu_3O_{8+\delta}$. Representation *a* emphasizes the Cu–O and Pb–O bonding scheme, and representation *b* emphasizes the manner in which Cu–O and Pb–O coordination polyhedra are arranged.

The range of oxygen contents possible for these compounds is remarkable. $Pb_2Sr_2YCu_3O_{8+\delta}$, $\delta = 0$, for example, can be oxidized by heating in O_2 to temperatures below 500 °C for short times (2–4 h) to δ values of ~1.6, retaining the same basic crystal structure. We have observed values as large as $\delta = 1.8$ for $Pb_2Sr_2Y_{0.75}Ca_{0.25}Cu_3O_{8+\delta}$. Oxidation at temperatures higher than 500 °C, or for longer reaction periods, generally results in decomposition to the $SrPbO_3$-based perovskite. Powder samples of $Pb_2Sr_2YCu_3O_{8+\delta}$ with large values of δ are not superconducting. Single crystals of the $Pb_2Sr_{2+x}Ln_xCu_3O_{8+\delta}$ type are superconductors with transition temperatures between 10 and 70 K. These crystals may have non-zero values of δ but have not yet been fully characterized. The range of T_cs observed suggests a complex and interesting relationship between T_c, δ and the Sr:Ln ratio.

Powder X-ray diffraction indicates that the new phases have an orthorhombic unit cell which is based on a many-layer perovskite structure. The characteristic X-ray pattern for the prototype compound $Pb_2Sr_2YCu_3O_8$ is presented in Table 1. The compound deviates only slightly from tetragonal symmetry. The simplest cell consistent with the X-ray pattern is *c*-centred, with lattice parameters $a = 5.40$, $b = 5.43$, and $c = 15.74$ Å. Systematic absences are consistent with a *c*-centred cell down to the detectability limit of 1% maximum intensity. The orthorhombic cell gives an excellent fit to the powder diffraction pattern but a hint of a shoulder on the high 2θ side of the 314 reflection indicates that the true symmetry may be weakly monoclinic. Although the lattice parameters for this family of compounds are very similar to those reported for $TlBa_2Ca_2Cu_3O_8$ (ref. 3), the crystal structures are quite different. Electron microscope investigations indicate that for some crystals, weak (but sharp) reflections are present which violate the *c*-centring. Furthermore, these studies show the presence of long-period, long-range-ordered superlattices in the *a*–*b* plane, suggesting that a variety of structural distortions and stoichiometry-driven atom-ordering schemes can occur.

The crystal structure of compounds in this family, determined for a superconducting Nd-based single crystal of approximate stoichiometry $Pb_2Sr_{2.24}Nd_{0.76}Cu_3O_{8+\delta}$ (determined by structure refinement) is shown in Fig. 1. The crystal employed in the structural determination was twinned, as expected from the pseudo-tetragonal symmetry. The atomic coordinates are reported in the *c*-centred orthorhombic cell to be consistent with the powder data, but a primitive cell with *a* and *b* rotated by 45° and reduced by $\sqrt{2}$ gives an equally good description of the single-crystal data. The very small scattering cross-section of oxygen precludes determination of δ by refinement. The data are well fitted by the structural model (refinement parameter $R = 3.7\%$), but a microscopic explanation of the orthorhombic symmetry is not apparent; if the origin is primarily in the oxygen sublattice we would not be able to detect it in the X-ray structure determination.

The basis of the structure comprises infinite planes of corner-shared CuO_5 pyramids separated by eight-coordinate rare-earth atoms, as are common to all the presently known copper-based superconductors with $T_c > 50$ K. The four in-plane copper-oxygen distances are ~1.9 Å, and the distance to the apical oxygen is ~2.3 Å, both of which are very similar to those observed in $YBa_2Cu_3O_7$. The structural components unique to the new class of materials are the PbO-CuO_δ-PbO planes shown in the centre of the Fig. 1. For $\delta = 0$, Pb has a distorted flattened square pyramid coordination (sharing edges with adjacent pyramids), with the lone pair pointing toward the vacant sixth site of the coordination octahedron. The PbO_5 pyramids are separated by a single copper layer, which, for $\delta = 0$, is oxygen-free, and displays an O–Cu–O coordination characteristic of Cu^{1+} (Cu–O distance ~1.8 Å), as is observed in non-superconducting $YBa_2Cu_3O_6$. During the low-temperature oxidation process, oxygen is apparently accommodated in this copper layer, resulting in a large expansion of the *c* axis. The PbO_5 and CuO_5 pyramidal planes are joined by the common oxygens at their apices. The Sr atoms are coordinated to nine oxygens, as in (La,

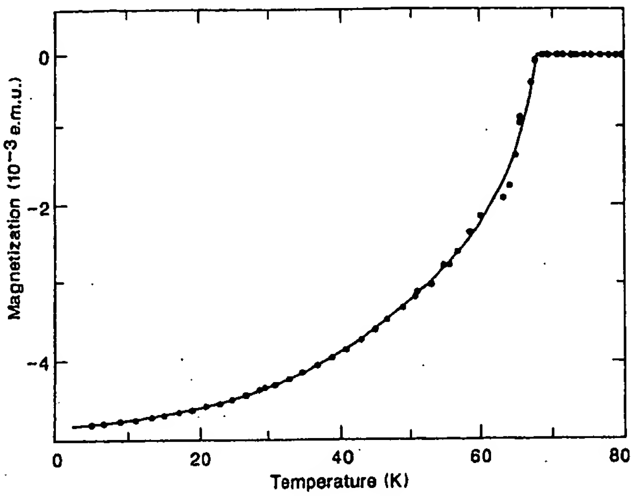

Fig. 2 Magnetization data (d.c. field-cooled at 25 Oe) for $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$.

Sr)CuO_4, and the Ln site is eight-coordinate, as in the $LnBa_2Cu_3O_7$ family, sandwiched between the CuO_5 pyramidal planes. In the superconducting compound $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_{8+\delta}$, Ca partially substitutes for Y in the eight-coordinate site.

The crystal structures of all the known copper-oxide-based superconductors are generally described as many-layered perovskites. The similarities and differences among them are most easily illustrated in terms of the stacking sequences of rocksalt-like (AO) and perovskite-like (BO_2) layers[2]. Taking, for example, representatives from the superconductor families that have double CuO_5 pyramidal layers, the stacking sequences are:

$Pb_2Sr_2(Y, Ca)Cu_3O_{8+\delta}$
-(Y, Ca)-CuO_2-SrO-PbO-CuO_δ-PbO-SrO-CuO_2-(Y, Ca)-

$Tl_2Ba_2CaCu_2O_8$
-Ca-CuO_2-BaO-TlO-TlO-BaO-CuO_2-Ca-

$YBa_2Cu_3O_{6+\delta}$
-Y-CuO_2-BaO-CuO_δ-BaO-CuO_2-Y-

Table 1 Characteristic X-ray powder diffraction pattern for $Pb_2Sr_2YCu_3O_8$

hkl	*d*	I/I_0	*hkl*	*d*	I/I_0
001	15.74	7	116	2.164	11
002	7.87	3	025	2.057	12
003	5.25	2	205	2.050	10
004	3.94	10	008	1.967	7
110	3.831	11	220	1.915	25
111	3.722	24	118, 009	1.750	2
112	3.444	1	027, 207	1.730	1
005	3.148	11	224	1.722	2
113	3.094	11	130	1.717	2
114	2.745	100	310, 131	1.708	3
020	2.717	43	311	1.699	2
200	2.701	43	225	1.636	3
021	2.677	7	133	1.632	3
201	2.662	7	313	1.625	1
006	2.623	6	028	1.593	11
023	2.412	1	208, 119	1.591	11
203	2.401	1	134	1.574	18
024	2.236	2	314	1.568	14
204	2.227	1			

Cu Kα radiation, 0–60° 2θ *c*-centred orthorhombic cell, preliminary indexing, true symmetry may be weakly monoclinic. Lattice parameters $a = 5.4019(15)$, $b = 5.4333(15)$, $c = 15.7388(33)$.

The new superconductors, then, can be seen to be intimately related in structure to those previously described. They can be considered as related to $Tl_2Ba_2CaCu_3O_8$ by insertion of a single CuO_δ layer between adjacent polarizable AO layers, or related to $YBa_2Cu_3O_{6+\delta}$ by sandwiching of the CuO_δ 'chain' layer by two PbO layers. We believe that it is the electronic screening of the CuO_2 planes from the CuO_δ layers by the PbO layers that makes the new superconductors of considerable interest. Furthermore, we expect these materials to be even more anisotropic in their physical properties than those previously known, as the double pyramidal CuO_2-A-CuO_2 layers are widely separated.

Superconducting properties

We have studied the composition dependence of the superconducting properties of compounds in the series $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_8$ for $0 \leq x \leq 0.75$, by estimating the flux expulsion measured on cooling in a field of 25 Oe in a d.c. SQUID magnetometer (S.H.E. model 905). The greatest flux expulsion occurs for $x = 0.5$, and is ~20% of the ideal value (see Fig. 2). Because flux becomes trapped in the pores of these low-density ceramics, this is an underestimate of the true volume fraction of superconductivity. For $x \geq 0.5$, the materials were not entirely single-phase, with one or more impurity peaks having a maximum intensity of 5% of the strongest peak in the powder X-ray pattern. This, coupled with the estimate of the volume fraction of superconductivity, suggests that the optimal superconducting composition may have x somewhat greater than 0.5. This could be achieved if different synthetic methods can be found that allow a larger range of solid solution to be attained. We have measured the normal-state susceptibility (in a 20-kOe field) for temperatures below 400 K of apparently single-phase samples (no unindexed X-ray lines to 0.5% maximum intensity) of the non-superconducting endmember $Pb_2Sr_2YCu_3O_8$ and superconducting $Pb_2Sr_2Y_{0.625}Ca_{0.375}Cu_3O_8$. The susceptibility of the superconductor (χ) is essentially temperature independent ($\chi \approx 1 \times 10^{-4}$ e.m.u. per mole formula unit), with only a slight decrease at low temperatures. This temperature dependence is similar to that of high-quality $YBa_2Cu_3O_7$, and is characterized by the absence of a Curie-Weiss contribution. Furthermore, this supports our conclusion that the copper atoms between the PbO layers are Cu^{1+}. Post-oxidation at 500 °C results in oxidation of this copper to magnetic Cu^{2+}. $Pb_2Sr_2YCu_3O_8$ appears to be magnetic (−0.5 μB per Cu atom), but further studies are necessary to clarify whether this is intrinsic or is due to the presence of highly magnetic impurity phases that are undetectable by X-ray diffraction.

Figure 3 shows the temperature dependence of the resistivity for a single crystal of $Pb_2Sr_2Dy_{1-x}Ca_xCu_3O_{8+\delta}$. The midpoint of the superconducting transition is at 51.5 K (indicated by an arrow in Fig. 3), although there is a small foot which gives a zero-resistance T_c of 46 K. Above T_c the temperature

Table 2 Crystallographic data for $Pb_2Sr_{2.24}Nd_{0.76}Cu_3O_{8+\delta}$

Atom	Position	*x*	*y*	*z*	B_{iso}[Å^2]
Pb	4l	1/2	0	0.38858 (4)	1.09 (2)
Sr	4k	0	0	0.22184 (9)	0.74 (4)
Nd, Sr*	2a	0	0	0	0.69 (3)
Cu1	2d	0	0	1/2	0.86 (9)
Cu2	4l	1/2	0	0.11074 (13)	0.46 (5)
O1	4l	1/2	0	0.2546 (8)	1.5 (5)
O2	4k	0	0	0.384 (3)	13 (5)
O3	8m	1/4	1/4	0.0995 (5)	0.9 (3)

Orthorhombic cell (pseudotetragonal substructure); $a = 5.435(1)$Å, $b = 5.463(1)$Å, $c = 15.817(3)$Å; space group *Cmmm*, $z = 2$; observed reflections 707, $R_w = 0.037$.

* Mixed occupancy site: 0.24(1) Sr, 0.76(1) Nd.

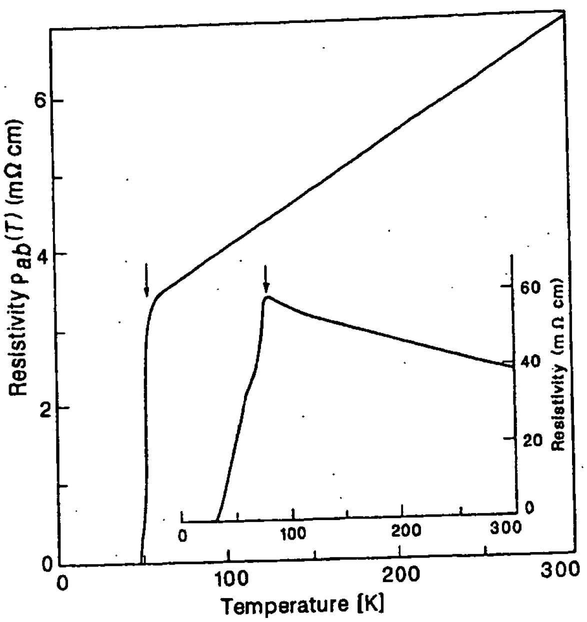

Fig. 3 Resistivity in the a-b plane as a function of temperature for a single crystal of $Pb_2Sr_2(Dy,Ca)Cu_3O_{8+\delta}$. Inset, typical temperature-dependent resistivity for a polycrystalline sample of $Pb_2Sr_2(Y,Ca)Cu_3O_8$.

dependence is fairly linear, but near T_c there is a region of positive curvature which, along with the resistivity foot, we attribute to small inhomogeneities in the metal and/or oxygen distribution. The scale of the resistivity is a factor of ten greater than for previous oxide superconductors. It is not yet clear whether this is an intrinsic property.

A typical resistivity curve for a ceramics sample is shown in the inset to Fig. 3, illustrating the typically broad transitions observed. The transition in this sample begins at 79 K (arrow) but zero resistance is achieved (within instrumental accuracy) as 32 K. Note that the resistivity scale is again quite high. We attribute the breadth of the transition and the negative normal-state temperature coefficient to inhomogeneity in the metal and/or oxygen distribution, rather than to exogenous phases at the grain boundaries. The behaviour of this system seems to be very similar to that of $(La,Sr)_2CuO_4$ (ref. 4).

Electronic aspects

Given that the average formal copper valence of previously known superconductors has always been greater than +2, the new superconductors are unique and, at first sight, anomalous. For the series $Pb_2Sr_2Y_{1-x}Ca_xCu_3O_8$, the average formal copper valence increases from 1.67 in the non-superconducting $x=0$ member to ~1.92 at the maximum Ca concentration studied. At our current estimate of the optimal superconducting composition ($x=0.5$), the average formal valence is 1.83. The linear coordination of the copper atom sandwiched between the PbO sheets, characteristic of Cu^{1+}, and the probable electronic isolation of this layer from the conducting CuO pyramidal planes, imply that the formal charge formulation becomes $Pb_2Sr_2YCu^{1+}Cu_2^{2+}O_8$ in the non-superconducting compound. When Ca is substituted for Y, we propose that holes are accommodated only in the CuO_5 planes, and at the $x=0.5$ stoichiometry the formal charge formulation becomes $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu^{1+}Cu_2^{2.25+}O_8$, which is consistent with the current assumption for previously known high-T_c materials that holes are present in the CuO_5 pyramidal planes.

For $Pb_2Sr_2ACu_3O_{8+\delta}$ compounds with $\delta>0$, excess oxygen must be accommodated near the Cu^{1+} planes, and a more complex hole-doping scheme may be operating. We expect that in that case the compound does not respond in a simple fashion to the change in charge through doping of a rigid band; the oxygen inserted in the bonding neighbourhood of the reduced Cu and Pb ions may create the electronic states in which the charge is partly or fully accommodated.

This new family of compounds has a unique crystal structure, yet it also reflects a concept common to all copper-oxide-based superconductors. By now it is well established that superconductivity is associated with layers of Cu-O octahedra, pyramids and squares. The remaining structural building blocks are seen as the electron acceptors which induce the holes necessary for superconductivity in the Cu-O layers. For $YBa_2Cu_3O_{6+\delta}$, for example, we have shown in detail how the CuO_δ chains act as charge reservoirs, and how superconductivity depends on charge transfer between chains and planes[5].

To illustrate the concept of local charge distribution, one may rewrite the formulae of the high-T_c copper-oxide superconductors as follows: $YBa_2Cu_2O_6[CuO_\delta]$; $Sr_2CaCu_2O_6[Bi_2O_2]$; $Ba_2CaCu_2O_6[Tl_2O_2]$; $Sr_2(Y,Ca)Cu_2O_6[Pb_2CuO_{2+\delta}]$; where the structural components in square brackets act as reservoirs which control the charge on the superconducting Cu-O planes. The PbO-CuO_δ-PbO reservoir layer is likely to be exceptionally flexible in accommodation of charge, and we therefore expect that a relationship between T_c and oxygen stoichiometry as unusual as that for $YBa_2Cu_3O_{6+\delta}$ will eventually be observed. The wide ranges of metal-atom and oxygen-atom stoichiometries in this new family of superconductors are of considerable interest, and warrant further study with the aim of understanding and optimizing the superconducting properties.

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